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(57) Abrégé/Abstract:

A low-molecular weight nitrite rubber having narrower molecular weight distributions than those known in the art can be prepared by olefin metathesis.



Abstract

A low-molecular weight nitrile rubber having narrower molecular weight distributions than those known in the art can be prepared by olefin metathesis.

Process for the Metathesis of Functionalized Polymers

Field of the Invention.

The present invention relates to nitrile rubber polymers having lower molecular weights and narrower molecular weight distributions than those known in the art.

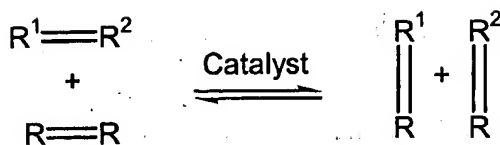
Background of the Invention

Nitrile rubber (NBR), a co-polymer of a conjugated diene and an unsaturated nitrile, is a specialty rubber which has very chemical resistance, and excellent oil resistance. Coupled with the high level of mechanical properties of the rubber (in particular the high resistance to abrasion) it is not surprising that NBR has found widespread use in the automotive (seals, hoses, bearing pads), electrical (cable sheathing), mechanical engineering (wheels, rollers) and footwear industries, amongst others.

Commercially available NBR is manufactured by emulsion polymerization. The monomers are emulsified in water, a free radical-generating catalyst is added and the mixture is agitated whilst a constant temperature is maintained. After the desired degree of polymerization is reached, a shortstop and stabilizers are added to the reaction system causing termination of the polymerization process. Generally, NBR obtained by this process has a Mooney viscosity in the range of from about 30 to about 90, an Mw in the range of from about 250,000 to about 350,000, an Mn in the range of from about 80,000 to about 150,000 and a polydispersity index greater than about 3.2.

In addition, so-called "liquid NBR" having a very low Mooney viscosity and a low molecular weight can be produced by adding the shortstop agent early in the reaction process. As in the case of regular NBR, the resulting liquid NBR has a polydispersity greater than 3.0.

Karl Ziegler's discovery of the high effectiveness of certain metal salts, in combination with main group alkylating agents, to promote olefin polymerization under mild conditions has had a significant impact on chemical research and production to date. It was discovered early on that some "Ziegler-type" catalysts not only promote the proposed coordination-insertion mechanism but also effect an entirely different chemical process, that is the mutual exchange (or metathesis) reaction of alkenes

**Figure 1**

Acyclic diene metathesis (or ADMET) is catalyzed by a great variety of transition metal complexes as well as non-metallic systems. Heterogeneous catalyst systems based on metal oxides, sulfides or metal salts were originally used for the metathesis of olefins. However, the limited stability (especially towards hetero-substituents) and the lack of selectivity resulting from the numerous active sites and side reactions are major drawbacks of the heterogeneous systems.

Homogeneous systems have also been devised and used to effect olefin metathesis. These systems offer significant activity and control advantages over the heterogeneous catalyst systems. For example, certain Rhodium based complexes are effective catalysts for the metathesis of electron-rich olefins.

The discovery that certain metal-alkylidene complexes are capable of catalyzing the metathesis of olefins triggered the development of a new generation of well-defined, highly active, single-site catalysts. Amongst these, Bis-(tricyclohexylphosphine)-benzylidene ruthenium dichloride (commonly known as Grubb's catalyst) has been widely used, due to its remarkable insensitivity to air and moisture and high tolerance towards various functional groups. Unlike the molybdenum-based metathesis catalysts, this ruthenium carbene catalyst is stable to acids, alcohols, aldehydes and quaternary amine salts and can be used in a variety of solvents (C_6H_6 , CH_2Cl_2 , THF, *t*-BuOH). The most commonly-used catalysts are based on Mo, W and Ru.

The use of transition-metal catalyzed alkene metathesis has since enjoyed increasing attention as a synthetic method. Research efforts have been mainly focused on the synthesis of small molecules, but the application of olefin metathesis to polymer synthesis has allowed the preparation of new polymeric material with unprecedented properties (such as highly stereoregular poly-norbornadiene).

The utilization of olefin metathesis as a means to produce low molecular weight compounds from unsaturated elastomers has received growing interest. The principle for the molecular weight reduction of unsaturated polymers is shown in Figure 2. The use of an appropriate catalyst allows the cross-metathesis of the unsaturation of the polymer with the co-olefin. The end result is the cleavage of the polymer chain at the unsaturation sites and the generation of polymer fragments having lower molecular weights. In addition, another effect of this process is the "homogenizing" of the polymer chain lengths, resulting in a reduction of the polydispersity. From an application and processing stand point, a narrow molecular weight distribution of the raw polymer results in improved physical properties of the vulcanized rubber, whilst the lower molecular weight provides good processing behavior.

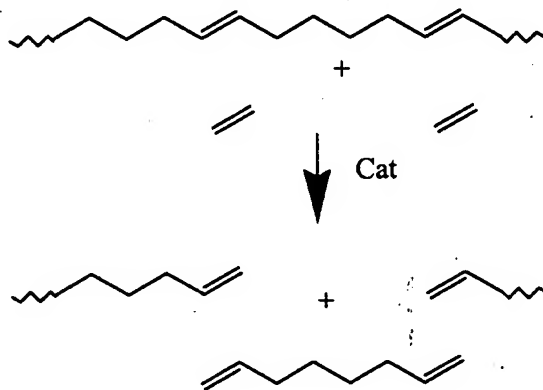


Figure 2 Metathesis of Partially Unsaturated Polymer

The so-called "depolymerization" of copolymers of 1,3-butadiene with a variety of co-monomers (styrene, propene, divinylbenzene and ethylvinylbenzene, acrylonitrile, vinyltrimethylsilane and divinyltrimethylsilane) in the presence of classical Mo and W catalyst system has been investigated. Similarly, the degradation of a nitrile rubber using WCl_6 and SnMe_4 or $\text{PhC}\equiv\text{CH}$ co-catalyst was reported in 1988. However, the focus of such research was to produce only low molecular fragments which could be characterized by conventional chemical means and contains no teaching with respect to the preparation of low molecular weight nitrile rubber polymers. Furthermore, such processes are non-controlled and produce a wide range of products.

The catalytic depolymerization of 1,4-polybutadiene in the presence of substituted olefins or ethylene (as chain transfer agents) in the presence of well-defined Grubb's or Schrock's catalysts is also possible. The use of Molybdenum or Tungsten compounds of the general structural formula $\{M(=NR_1)(OR_2)_2(=CHR)\}$; $M = Mo, W$ to produce low molecular weight polymers or oligomers from gelled polymers containing internal unsaturation along the polymer backbone was claimed in US 5,446,102. Again, however, the process disclosed is non-controlled, and there is no teaching with respect to the preparation of low molecular weight nitrile rubber polymers.

10 Summary of the Invention

We have now discovered that a low molecular weight nitrile rubber having narrower molecular weight distributions than those known in the art can be prepared by olefin metathesis. Rubbers having a narrow molecular weight distribution have certain advantages over those having a broad molecular weight distribution, one of these being that they have improved physical properties, resulting, for example, in better processability of the rubber.

Thus, one aspect of the disclosed invention is a nitrile rubber having a molecular weight (M_w) in the range of from about 25,000 to about 200,000, a Mooney viscosity (ML 1+4 100) of less than about 25, and a MWD (or polydispersity index) of less than about 2.5.

Description of the Invention

As used throughout this specification, the term "nitrile rubber" is intended to have a broad meaning and is meant to encompass a copolymer of a conjugated diene and an unsaturated nitrile.

The conjugated diene may be a C_4 - C_6 conjugated diene. Non-limiting examples of suitable such conjugated dienes may be selected from the group comprising butadiene, isoprene, piperylene, 2,3-dimethyl butadiene and mixtures thereof. The preferred C_4 - C_6 conjugated diene may be selected from the group comprising butadiene, isoprene and mixtures thereof. The most preferred C_4 - C_6 conjugated diene is butadiene.

The unsaturated nitrile may be a C₃-C₅ α,β-unsaturated nitrile. Non-limiting examples of suitable such C₃-C₅ α,β-unsaturated nitriles may be selected from the group comprising acrylonitrile, methacrylonitrile, thacrylonitrile and mixtures thereof. The most preferred C₃-C₅ α,β-unsaturated nitrile is acrylonitrile.

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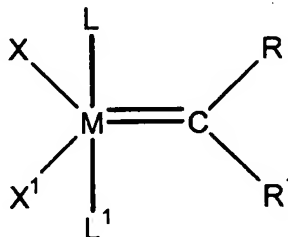
Preferably, the copolymer comprises from about 40 to about 85 weight percent of the copolymer of bound conjugated diene and from about 15 to about 60 weight percent of the copolymer of bound unsaturated nitrile. More preferably, the copolymer comprises from about 60 to about 75 weight percent of the copolymer of bound conjugated diene and from about 25 to about 40 weight percent of the copolymer of bound unsaturated nitrile. Most preferably, the copolymer comprises from about 60 to about 70 weight percent of the copolymer of bound conjugated diene and from about 30 to about 40 weight percent of the copolymer of bound unsaturated nitrile.

15 Optionally, the copolymer may further comprise a bound unsaturated carboxylic acid. Non-limiting examples of suitable such bound unsaturated carboxylic acids may be selected from the group comprising fumaric acid, maleic acid, acrylic acid, methacrylic acid and mixtures thereof. The bound unsaturated carboxylic acid may be present in an amount of from about 1 to about 10 weight percent of the copolymer, with
20 this amount displacing a corresponding amount of the conjugated diolefin.

Further, a third monomer may be used in production of the nitrile polymer. Preferably, the third monomer is an unsaturated mono- or di-carboxylic acid or derivative thereof (e.g., esters, amides and the like).

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The metathesis reaction can be catalysed by compounds of formula I, II or III; as shown below :



Formula I

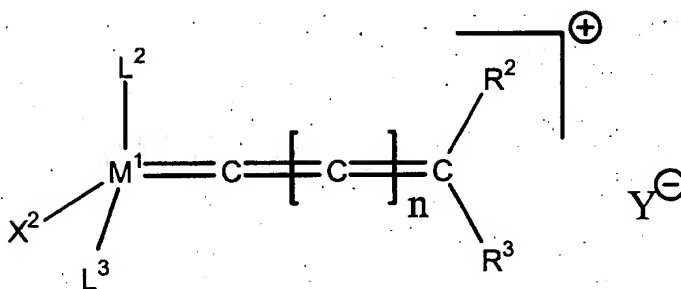
wherein:

M is Os or Ru;

R and R¹ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

X and X¹ are independently selected anionic ligands; and

L and L¹ are, independently, ligands selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines having up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibines, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines; optionally, L and L¹ can be linked to one another to form a bidentate neutral ligand wherein at least one of the above-mentioned functional groups is present.



Formula II

wherein:

M¹ is Os or Ru;

R² and R³ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

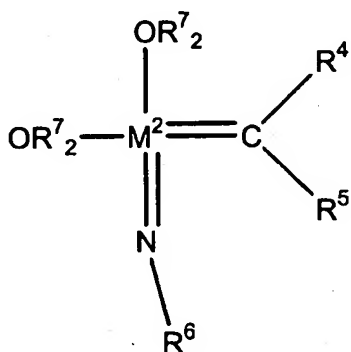
X² is selected from any anionic ligand; and

L² is a neutral π -bonded ligand, preferably but not limited to arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

L³ is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three

aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

- 5 Y^- is a non-coordinating anion;
 n is an integer in the range of from 0 to 5;



Formula III

wherein

- 10 M^2 is Mo or W

R^4 , R^5 are, independently, hydrogen or a hydrocarbon selected from the group consisting of C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} alkyl, aryl, C_1 - C_{20} carboxylate, C_1 - C_{20} alkoxy, C_2 - C_{20} alkenyloxy, C_2 - C_{20} alkynyloxy, aryloxy, C_2 - C_{20} alkoxycarbonyl, C_1 - C_{20} alkylthio, C_1 - C_{20} alkylsulfonyl and C_1 - C_{20} alkylsulfinyl;

- 15 R^6 and R^7 are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof.

- 20 Catalysts of Formula I are preferred. More preferably, catalysts of Formula I wherein L and L^1 are trialkylphosphines, X and X^1 are chloride ions and M is Ruthenium are preferred.

- 25 The amount of catalyst employed in the metathesis reaction will depend upon the nature and activity of the catalyst in question. Typically, the ratio of catalyst to NBR is in the range of from about 0.005 to about 5, preferably in the range of from about 0.025 to about 1 and, more preferably, in the range of from about 0.1 to about 0.5.

The metathesis reaction is carried out in the presence of a co-olefin. The co-olefin may be a hydrocarbon or it may be functionalised, with the caveat that it should not inactivate the metathesis catalyst or otherwise interfere with the reaction. Preferred olefins include, but are not limited to, C₂ to C₁₆ linear or branched olefins such as ethylene, isobutene, styrene or 1-hexene. Where the co-olefin is a liquid (such as 1-hexene), the amount of co-olefin employed is in the range of from about 1 to about 50 weight %; preferably in the range of from about 10 to about 30 weight %. Where the co-olefin is a gas (such as ethylene) the amount of co-olefin employed is such that it results in a pressure in the reaction vessel in the range of from about 3 to about 3600 psi, preferably in the range of from about 15 to about 1500 psi and, more preferably, in the range of from about 75 to about 600 psi.

The metathesis reaction can be carried out in any suitable solvent which does not inactivate the catalyst or otherwise interfere with the reaction. Preferred solvents include, but are not limited to, dichloromethane, benzene, toluene, tetrahydrofuran, methyl ethyl ketone, cyclohexane and the like. The most preferred solvent is monochlorobenzene (MCB). In certain cases the co-olefin can itself act as a solvent (for example, 1-hexene), in which case no other solvent is necessary.

The concentration of NBR in the reaction mixture is not critical but, obviously, should be such that the reaction is not hampered if the mixture is too viscous to be stirred efficiently, for example. Preferably, the concentration of NBR is in the range of from about 1 to about 40%, most preferably in the range of from about 6 to about 15%.

The metathesis reaction is carried out at a temperature in the range of from about 20 to about 140°C; preferably in the range of from about 60 to about 120°C.

The reaction time will depend upon a number of factors, including cement concentration, amount of catalyst used and the temperature at which the reaction is performed. The metathesis is complete within the first two hours under typical conditions. The progress of the metathesis reaction may be monitored by standard analytical techniques, for example using GPC or solution viscosity.

The Mooney viscosity of the rubber was determined using ASTM test D1646.

For a typical product the Mn is about 30,000 (compared to about 85,000 for the starting polymer) whilst the Mw is about 55,000 (compared to 300,000 for the starting polymer). As can be seen from Table 1, however, higher molecular weights (Mw) can also be obtained by manipulation of the experimental conditions (for example by lowering the catalyst loading). As expected, the molecular weight distribution falls from about 3.5 for the starting NMB feedstock to about 2.0 for the metathesized product. This is consistent with a more homogeneous range of polymer chain lengths and molecular weights.

A summary of the polymer properties for selected samples is shown in Table 1. The GPC results show up to a fivefold reduction in Mw and a narrowing of the polydispersity index to about 2.0.

Table 1 Summary of Polymer Properties

	MN	MW	MZ	PDI	Mooney Viscosity (ML 1+4 @ 100)
Starting NBR (Perbunan)	85000	296000	939000	3.50	35
Experiment 1	27000	54000	92000	2.00	2.5
Experiment 2	27000	53000	89000	1.98	-
Experiment 3	32000	66000	117000	2.06	-
Experiment 4	67000	134000	253000	2.00	-

Experimental Details

Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride (Grubb's metathesis catalyst), 1-hexene and monochlorobenzene (MCB) were purchased from Alfa, Aldrich Chemicals, and PPG respectively and used as received. Perbunan was obtained from Bayer Inc.

The metathesis reactions were carried out in a Parr high-pressure reactor under the following conditions:

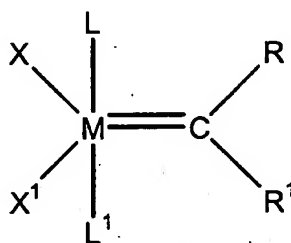
Cement Concentration 6 or 15%

Co-Olefin	Ethylene or 1-Hexene
Co-Olefin Concentration	Variable
Agitator Speed	600 rpm
Reactor Temperature	Variable
5 Catalyst Loading	Variable
Solvent	Monochlorobenzene
Substrate	Perbunan NT 3435 T
	Perbunan NT 3429 T

- 10 In a typical lab experiment, 200g of rubber was dissolved in 1133g of MCB (15% solid). The cement was then charged to the reactor and degassed 3 times with C_2H_4 (100 psi) under full agitation. The reactor was heated to desired temperature and 60mL of a monochlorobenzene solution containing Grubb's catalyst was added to the reactor. The temperature was maintained constant for the duration of the reaction. A cooling
- 15 coil connected to a temperature controller and a thermal sensor was used to regulate the temperature. The progress of the reaction was monitored using solution viscosity measurements for the 6% cements. At higher cement concentration, the reaction was assumed to be complete after 18 hours.

Claims

1. A process for the preparation of a nitrile rubber which comprises subjecting a nitrile rubber to metathesis in the presence of a co-olefin and a catalyst selected from the group consisting of Formula I, II and III :



Formula I

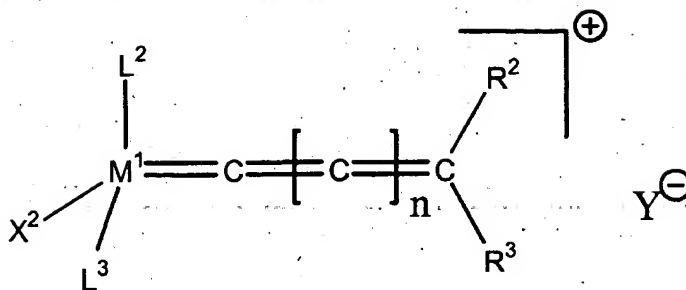
wherein:

M is Os or Ru;

- 10 R and R' are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxy carbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

X and X' are independently selected anionic ligands; and

- 15 L and L' are, independently, ligands selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines having up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxy carbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibines, ethers, amines, amides, imines, 20 sulfoxides, thioethers and pyridines; optionally, L and L' can be linked to one another to form a bidentate neutral ligand wherein at least one of the above-mentioned functional groups is present;



Formula II

wherein:

M¹ is Os or Ru;

R² and R³ are, independently, hydrogen or a hydrocarbon selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

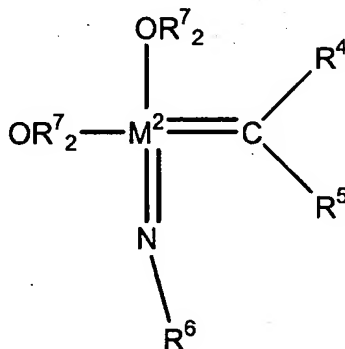
X² is selected from any anionic ligand; and

L² is a neutral π-bonded ligand, preferably but not limited to arene, substituted arene, heteroarene, independent of whether they are mono- or polycyclic;

L³ is a ligand selected from the group consisting of phosphines, sulfonated phosphines, fluorinated phosphines, functionalized phosphines bearing up to three aminoalkyl-, ammoniumalkyl-, alkoxyalkyl-, alkoxycarbonylalkyl-, hydroxycarbonylalkyl-, hydroxyalkyl- or ketoalkyl- groups, phosphites, phosphinites, phosphonites, phosphinamines, arsines, stibenes, ethers, amines, amides, imines, sulfoxides, thioethers and pyridines;

Y⁻ is a non-coordinating anion;

n is an integer in the range of from 0 to 5;



Formula III

wherein

M^2 is Mo or W

R^4 , R^5 are, independently, hydrogen or a hydrocarbon selected from the group consisting of C_2 - C_{20} alkenyl, C_2 - C_{20} alkynyl, C_1 - C_{20} alkyl, aryl, C_1 - C_{20} carboxylate, C_1 - C_{20} alkoxy, C_2 - C_{20} alkenyloxy, C_2 - C_{20} alkynyloxy, aryloxy, C_2 - C_{20} alkoxy carbonyl, C_1 - C_{20} alkylthio, C_1 - C_{20} alkylsulfonyl and C_1 - C_{20} alkylsulfinyl;

R^6 and R^7 are independently selected from any unsubstituted or halo-substituted alkyl, aryl, aralkyl groups or silicon-containing analogs thereof.

- 10 2. A process according to claim 1 wherein the metathesis catalyst is a compound of Formula I.
3. A process according to claim 2 wherein L and L^1 are trialkylphosphines, X and X^1 are chloride ions and M is ruthenium.
- 15 4. A process according to claim 1 wherein the ratio of catalyst to nitrile rubber is in the range of from about 0.005 to about 5.
5. A process according to claim 4 wherein the ratio of catalyst to nitrile rubber is in the range of from about 0.025 to about 1.
- 20 6. A process according to claim 5 wherein the ratio of catalyst to nitrile rubber is in the range of from about 0.1 to about 0.5.
- 25 7. A process according to claim 1 wherein the co-olefin is a C_2 to C_{16} linear or branched olefin.
8. A process according to claim 7 wherein the co-olefin is selected from the group consisting of ethylene, isobutene, styrene and 1-hexene.
- 30 9. A process according to claim 8 wherein the co-olefin is ethylene.
10. A process according to claim 1 wherein, if the co-olefin is a liquid, the amount employed is in the range of from about 1 to about 50 weight %.

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11. A process according to claim 10 wherein the amount of co-olefin employed is in the range of from about 10 to about 30 weight %.
- 5 12. A process according to claim 1 wherein, if the co-olefin is a gas, the amount employed is such that the resulting pressure in the reaction vessel is in the range of from about 3 to about 3600 psi
- 10 13. A process according to claim 12 wherein, if the co-olefin is a gas, the amount employed is such that the resulting pressure in the reaction vessel is in the range of from about 15 to about 1500 psi.
14. A process according to claim 13 wherein the amount of co-olefin employed is in the range of from about 75 to about 600 psi.
- 15 15. A process according to claim 1 wherein the process is carried out in an inert solvent selected from the group consisting of monochlorobenzene, dichloromethane, benzene, toluene, tetrahydrofuran, methyl ethyl ketone and cyclohexane.
- 20 16. A process according to claim 15 wherein the solvent is monochlorobenzene.
17. A process according to claim 1 wherein the concentration of nitrile rubber is in the range of from about 1 to about 40%.
- 25 18. A process according to claim 17 wherein the concentration of nitrile rubber is in the range of from about 6 to about 15%.
19. A process according to claim 1 wherein the metathesis reaction is carried out at a temperature in the range of from about 20 to about 140°C.
- 30 20. A process according to claim 19 wherein the metathesis reaction is carried out at a temperature in the range of from about 60 to about 120°C.